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Theoretical evaluation of thermodynamic quantities and differential scattering cross section of ionic Au-Cs melts using Blum's generalised Γ-parameter

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Abstract : Extensive evidence is available to prove that gold-caesium melt is ionic at 50 at % of Cs. Treating this melt as charged-hard-sphere mixture, Blum's generalised equations of asymmetric electrolytes have been used to compute the differential scattering cross section, static correlation functions and compressibility. It is found that the agreement between the calculated scattering cross section and the experimental values are excellent at 50 at % of Cs. A theoretical technique for the evaluation of the excess energy, the Helmholtz free energy and the entropy at different at % of Cs are described on the basis of this model. The value of the Γ-parameter found for this melt is similar in magnitude to that of molten salts.

Keywords : Γ-parameter, direct correlation function, total structure factor, neutron scattering lengths, Mean Spherical Model Approximation, excess properties.

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1. Introduction

From a consideration of specific conductivity (Schmutzler et *al* 1976), electromigration (Kruger and Schmutzler 1976), thermo-electric power (Schmutzler et *al* 1976), magnetic susceptibility (Freyland and Steinleitner 1976) of Cs-Au melt Martin et *al* (1980) pointed out that molten Cs-Au alloy consists of Cs^+ and Au^- ions. According to Hensel (1979), Martin and his coworkers (1980) and Evans and Telo-Da-Gamma (1980), it is well established that gold and caesium form an ionic compound around 50 at % of Cs. This assumption is supported by the difference in Pauling's electronegativities (Pauling 1960) of Cs and Au, and from the fact that at 50 atomic percent of Au there is a large decrease in volume from the ideal volume of mixing (Martin et *al* 1980). At this juncture, it may be mentioned that the amount of charge-transfer above the equiatomic concentration

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varies with the variation of Cs-concentration, i.e. partial charge-transfer takes place (Bosch *et al* 1978).

From charge conservation one can write,

$$x\Delta n_A+(1-x)\Delta n_B=0 \tag{1}$$

where x is the atomic fraction of metal A, Δn_A and Δn_B are the amounts of charge transferred from one metal to the other.

On the other hand, the partial direct correlation functions for asymmetric charged hard sphere mixtures for the most general case of arbitrary charge and size have been obtained by Blum in the primitive model of electrolytes under the Mean Spherical Model Approximation (MSMA) (Blum 1975, Hiroike 1977).

Hence the authors felt that Cs-Au melt is one such system for which the Blum's generalized theory of electrolytes can be applied to obtain the excess thermodynamic quantities (Rao and Satpathy 1988, Abernethy and Silbert 1982) and the structural properties (Blum 1975, Rao and Satpathy 1989).

2. Structural properties

Hiroike (1977) derived explicit expressions for the partial direct correlation functions and they can be conveniently written as

$$C_{ij}(r)=C^0_{ij}(r)-\frac{2e^2}{\epsilon_0 k_B T}[-Z_iN_j+X_i(N_i+X_i)-(\sigma_i/3)(N_i+\Gamma X_i)^2], \tag{2}$$

for the region $0 \leqq r \leqq \lambda=(\sigma_j-\sigma_i)/2$ when $\sigma_i < \sigma_j$.

$$\begin{aligned}C_{ij}(r)=C^0_{ij}(r)+\frac{e^2}{\epsilon_0 k_B T}\Bigg[&\frac{(\sigma_i-\sigma_j)}{r}\Big\{\frac{(X_i+X_j)}{4}[(N_i+\Gamma X_i)-(N_j+\Gamma X_j)]\\&-\frac{(\sigma_i-\sigma_j)}{16}[(N_i+\Gamma X_i+N_j+\Gamma X_j)^2-4N_iN_j]\Big\}-\{(X_i-X_j)(N_i-N_j)\\&+(X_i^2+X_j^2)\Gamma+(\sigma_i+\sigma_j)N_iN_j-\frac{1}{3}[\sigma_i(N_i+\Gamma X_i)^2+\sigma_j(N_j+\Gamma X_j)^2\}\\&+\Big\{\frac{X_i}{\sigma_i}(N_i+\Gamma X_i)+\frac{X_j}{\sigma_j}(N_j+\Gamma X_j)+N_iN_j-\frac{1}{2}[(N_i+\Gamma X_i)^2\\&+(N_j+\Gamma X_j)^2]\Big\}r+\{(6\sigma_i^2)^{-1}(N_i+\Gamma X_i)^2+(6\sigma_j^2)^{-1}\\&(N_j+\Gamma X_j)^2\}r^3\Bigg],\end{aligned}$$

for the region $\lambda \leqslant r < \sigma_{ij}$ when $\sigma_i < \sigma_j$. (3)

Here $C^0_{ij}(r)$ denotes the direct correlation function for the neutral hard-sphere mixture in the P-Y approximation and we use the expressions obtained by Lebowitz (1964). The $C_{ij}(r)$ out side the core is

$$C_{ij}(r)=-\frac{Z_iZ_j}{\epsilon_0 k_B T}\frac{}{r} \text{ for } \sigma_{ij} \leqslant r < \infty \tag{4}$$

where, Γ is the well known Blum's generalised inverse length parameter (Rao and Satpathy 1988, Abernethy and Silbert 1982) and the rest of the symbols have been explained well and are given in detail by Hiroike (1977) and by Rao and Satpathy (1988, 1989).

The Fourier Transformations (FT) of the above equations are straightforward and are simplified in working from for 1-1 type of salts (Rao and Satpathy 1989). The partial structure factors $S_{ij}(k)$'s are connected with $C_{ij}(k)$'s through Pearson-Rushbrooke's equations (Pearson and Rushbrooke 1957). The $S_{ij}(k)$'s are related to the total structure factor $S(k)$ as follows (Rao and Das 1987)

$$S(k)=\sum_{i=1}^{2}\sum_{j=1}^{2}(C_iC_j)^{1/2}\frac{f_i(k)f_j(k)}{c_1f_1^2(k)+c_2f_2^2(k)}S_{ij}(k) \tag{5}$$

Here $f_i(k)$ and $f_j(k)$ are atomic scattering factors if X-rays are used otherwise they are neutron scattering lengths, C_i the atomic fraction of the i-th species.

In this paper, we evaluate the neutron coherent scattering intensities from the computed total structure factors and these are compared with experimental values at 50 at % of Au. The equations related to the neutron coherent scattering intensities are as follows (Rao and Das 1987)

$$\frac{1}{N}\left(\frac{d\sigma}{d\Omega}\right)_{coh}=\langle b\rangle^2-\langle b\rangle^2+\langle b\rangle^2[1+4\pi\rho_0\int_0^{\alpha}\{g(r)-1\}r^2j_0(kr)dr]. \tag{6}$$

Here,

$$\langle b^2\rangle=C_1b_1^2+C_2b_2^2 \tag{7}$$

and

$$\langle b\rangle=C_1b_1+C_2b_2 \tag{8}$$

where $g(r)=\rho(r)/\rho_0$ is the pair correlation function, with ρ_0 as the mean number density and $\rho(r)$ is the local number density which is related to the scattering length as follows

$$\rho(r)=\frac{1}{\langle b\rangle^2}[C_1b_1^2\rho_{11}(r)+C_2b_2^2\rho_{22}(r)+2C_1b_1b_2\rho_{12}(r)]. \tag{9}$$

Here, b_1 and b_2 are the neutron coherent scattering lengths of the species 1 and 2. Scattering lengths used in the present case are $b_{Cs}=5.42\times10^{-13}$ cm and $b_{Au}=7.65\times10^{-13}$ cm (Martin *et al* 1980). Further in eq. (9), $\rho_{12}(r)$ is the atomic number density of atoms 2 at a distance r from the species 1. We give in Figure 1 the computed differential coherent scattering cross sections. The static correlation in densities of number and mass respectively, are related to $S_{ij}(k)$ as (Bhatia and Thorton 1970, Adams *et al* 1975).

$$S^{NN}(k)=C_1S_{11}(k)+C_2S_{22}(k)+2(C_1C_2)^{1/2}S_{12}(k) \tag{10}$$

$$S^{MM}(k)=\frac{1}{m^2}[m_1^2S_{11}(k)+m_2^2S_{22}(k)+2m^2S_{12}(k)] \tag{11}$$

where, m is the effective mass and is given by (Mansoori et *al* 1971).

$$m=m_1^{\sigma_1}m_2^{\sigma_2} \tag{12}$$

Here, m_1 and m_2 are the masses of the different species, respectively. The compressibility χ_T of the molten Au-Cs is obtained through the well-known equation (Simon and Deleuw 1978).

$$\lim_{k\to 0} S^{NN}(k)=\chi_T k_B T\rho_T \tag{13}$$

where, ρ_T is the total number density of the liquid alloy.

3. Thermodynamic quantities

The total entropy of the ionic melt can be written as (Abernethy and Silbert 1982, Rao and Satpathy 1988).

$$S_{tot}=S_{hs}+S_{ch} \tag{14}$$

where, S_{hs} is the entropy of neutral particles and S_{ch} is that due to charging process. The method of calculation of S_{hs} has been given in detail elsewhere.

The entropy due to coulomb interaction in the mean spherical model approximation (MSMA) is given by (Hiroike 1977, Rao and Satpathy 1988)

$$\frac{S_{ch}}{NK_B}=-\frac{\Gamma^3}{3\pi\rho_T} \tag{15}$$

is internal energy per unit volume due to the electrical charg defined as

$$E^{ex}=1/2\sum_{i,j=1}^{n}\rho_i\rho_j\int_{\sigma_{ij}} g_{ij}(r)v_{ij}(r)4\pi r^2dr \tag{16}$$

where, the interaction potential between i-th and j-th species is given by

$$v_{ij}(r)=\begin{cases}\infty & \text{for } r<\sigma_{ij}.\\ \dfrac{e^2}{\epsilon_0}Z_iZ_j & \text{for } r>\sigma_{ij}.\end{cases} \tag{17}$$

Here, $\sigma_{ij}=(\sigma_i+\sigma_j)/2$, ϵ_0 is the dielectric constant of the medium, and Z_i is the charge in electron units.

For the present melt, the eq. (15) can be written as (Hiroike 1977, Rao and Satpathy 1988)

$$E^{ex}=-\frac{e^2}{\epsilon_0}\left[\sum_{i=1}^{2}\frac{\rho_iZ_i^2}{1+\Gamma\sigma_i}+\frac{\nu\left\{\sum_{i=1}^{2}\rho_i\sigma_iZ_i(1+\Gamma\sigma_i)^{-1}\right\}}{1+\nu\left\{\sum_{i=1}^{2}\rho_i\sigma_i^3(1+\Gamma\sigma_i)^{-1}\right\}}\right]. \tag{18}$$

The excess Helmholtz free energy per unit volume via Kirkwood's charging process is given by (Hiroike 1977, Rao and Satpathy 1988)

$$F^{ex} = E^{ex} + (1/3)\frac{k_B T}{\pi}\Gamma^s. \tag{19}$$

4. Results and discussion

The present calculation is based on the following physically acceptable assumption

(i) It is experimentally well-established that at 50 at % of Cs the Au-Cs melt is fully ionised, and the amount of charge transfer 'Q' in the unit of elementary charge is given by

$$Q = Z_{Cs} = -Z_{Au}.$$

(ii) For the other concentrations of Cs, the partial charge transfer takes place, maintaining the charge coservation Bosch *et al* 1978, Pratap *et al* 1988

$$C_{Cs}\Delta Z_{Cs} + C_{Au}\Delta Z_{Au} = 0. \tag{20}$$

(iii) Along with others (Bhuiyan 1979, Evans and Telo De Gamma 1980) the dielectric constant is taken to be unity

The generalised Γ parameters at different concentrations have been solved numerically by the method already discussed (Rao and Satpathy 1988), using the best fitted σ_{ij}'s which are adjusted to match the experimental total structure factors (Martin *et al* 1980). It may be mentioned σ_{ij}'s should change slightly with the change of concentrations of Cs as the radius of the Wigner cell changes with concentrations (Pratap *et al* 1988). The values of Γ as calculated for different at % of Cs are found to vary from 5.4 to 9.5 nm^{-1}. The densities have been obtained from the formulae given by Martin *et al* (1980).

4.1. Structural properties and compressibility :

In this paper, we have presented the differential scattering cross section of the melts with 50 at % of Cs. It can be seen from Figure 1 that the calculated differential scattering cross section agrees very well in the first peak region. The pre-maxima which is found experimentally (Martin *et al* 1980) is sufficiently well-reproduced in the present calculations. The calculated positions and peak heights are given in Table 1 along with the experimental results. At this juncture, it may be pointed out that Evans and Telo Da Gamma (1980) also evaluated the structure factor using Waisman-Lebowitz solution (Waisman and Lebowitz 1972) and with an unphysical assumption of $\sigma_{Au} = \sigma_{Cs} = 3.15$ Å while the diameters differ by about 16% as given by Martin *et al* (1980). Such assumption made by Evans and Telo

Da Gamma (1980) made equations of Waisman and Lebowitz (1972) very simple otherwise their equations contain some seven parameters (Rao and Dasgupta 1987).

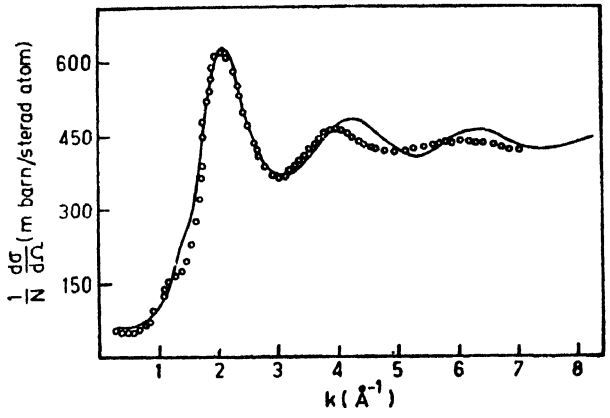

Figure 1. Coherent differential scattering cross section per atom of gold-caesium melts for 50 at % Cs at 913 K, OOOO experimental, ——— theoretical results.

Hence, their calculations are in fact very crude. Further, their results are of qualitative nature and there is a wide disagreement between the calculated and experimental first peak heights and also at low k-values. They also get a phase shift in their $S(k)$ while in the present computations no unphysical assumptions

Table 1. Typical data of the coherent differential scattering cross section and mass-mass correlation functions.

Cs-concentration (at %)			$\frac{1}{N}\frac{d\sigma}{d\Omega}\Big\|_{coh}$		$S^{MM}(k)$	
			Position Å^{-1}	Height (m barn/ sterad atom)	Position Å^{-1}	Height
50	Expt.	Pre-max	1.25	160.0	—	—
		1st max	2.00	610.0	—	—
	Present	Pre-max	1.30	215.0	1.45	1 48
		1st max	2.05	625.0	2.10	3.13

need to be made. The $S^{NN}(k)$ at 50% Cs is given in Figure 2. The $S^{NN}(k)$ shows the usual features of the total structure factors. Thus at large k, $S^{NN}(k)$ becomes unity and show a conspicuous first peak. The details of $S^{NN}(k)$ are given in Table 2. It is gratifying to note that $S^{NN}(k_{max})$ in excellent agreement with that of Martin *et al* (1980). In Figure 3, we clearly see that mass-mass correlation function shows a small shoulder to the left of the first peak corresponding to the pre-maximum. It may be mentioned that the pre-maxima is excellently manifested

in the mass-mass correlation function. This clearly indicates the ionic nature of the melt. It may be observed that the first peak of $S^{MM}(k)$ is broad even though

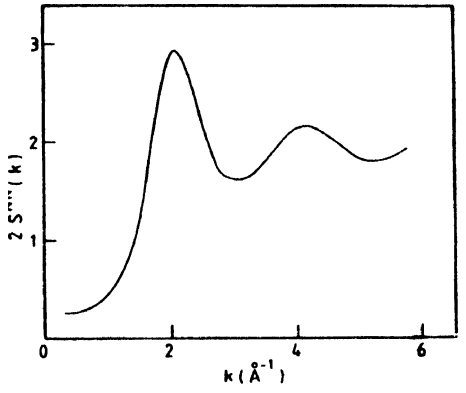

Figure 2. Number-number correlation functions of gold-caesium melts for 50 at % of Cs at 913 K.

comparatively higher than the peak height of $S^{NN}(k)$. In Table 1, the features of $S^{MM}(k)$ are given in detail. It may be recalled that in the present calculations,

Table 2. Structural details of $S^{NN}(k)$, long wave length data and isothermal compressibilities.

Cs-concentration (at %)	$S^{NN}(k_{max})$ Position (Å⁻¹)	Height	$S_{11}(0)$	$S_{22}(0)$	$S_{12}(0)$	$S^{NN}(0)$	$\chi_T \times 10^{-12}$ (cm² dyn⁻¹)
50	2.05	1.50	0.0625	0.0640	0.0615	0.125	45.93

the static correlation functions are obtained from detailed values of $S_{11}(k)$, $S_{22}(k)$ and $S_{12}(k)$. The compressibilities obtained by eq. (13) are given in Table 2,

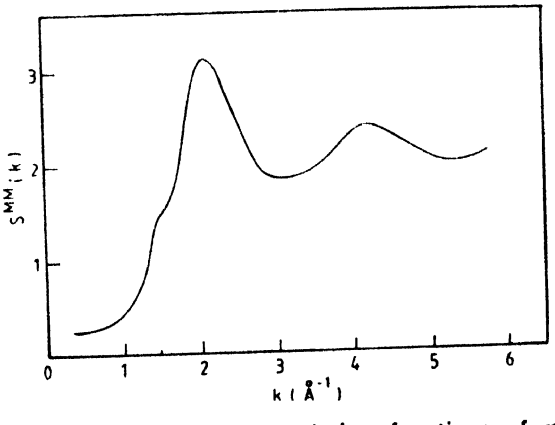

Figure 3. Mass-mass correlation functions of gold-caesium for 50 at % of Cs at 913 K.

unfortunately, no experimental data is there for comparison. At this juncture, it may be mentioned that for uni-univalent salts we have (Rao and Dasgupta 1987)

$$S_{11}(0)=S_{22}(0) \simeq S_{12}(0). \tag{21}$$

Table 3. Thermodynamic quantities of Au-Cs melts for different concentration of Cs.

Cs-concentration (at %)	Temp. (K)	σ_{ii} (1) Cs (Å)	σ_{ii} (1) Au (Å)	E^{ex}/Nk_BT	F^{ex}/Nk_BT	S_{hs}/Nk_B	S_{ch}/Nk_B	S/Nk_B	S_{ch}/S
50	913.0	2.75	3.15	−45.68	−41.58	14.59	−4.09	10.50	0.38
53	913.0	2.75	3.15	−40.09	−36.20	14.65	−3.90	10.75	0.36
55	913.0	2.75	3.15	−36.81	−32.98	14.78	−3.83	10.95	0.34
60	873.0	3.15	3.40	−27.79	−24.98	14.47	−2.81	11.66	0.24
70	773.0	3.15	3.45	−18.85	−16.78	14.97	−2.07	12.90	0.15
75	723.0	3.10	3.22	−15.88	−14.08	15.14	−1.80	13.34	0.13
80	693.0	3.10	3.24	−11.87	−10.37	15.28	−1.50	13.78	0.10

(1) Best fitted diameters.

This is found to be true in the present melt as well (vide Table 2), indicating that the alloy at 50 at % of Cs is salt-like and uni-univalent in character. The compressibility sum rule for fused salts can be written as

$$\lim_{k\to 0} S_{ij}(k) = [\rho_i \rho_j]^{1/2} k_B T \chi_T. \tag{22}$$

Eq. (22) is also true for the present melts.

4.2. *Thermodynamic properties :*

In this section, we discuss about the excess thermodynamic quantities, mainly. the entropy which is an important quantity to study the degree of ordering of the melt. The total entropy per particle S/Nk_B of the Au-Cs melts for different at % of Cs have been calculated using the best fitted σ_{ij}'s and Γ, obtained from experimental total structure factor (Martin *et al* 1980). The different contributions of the entropy are shown in Table 3. The excess internal energy E^{ex}/Nk_BT and Helmholtz free energy F^{ex}/Nk_BT, are calculated from eqs. (18) and (19) are given in Table 3. It can be seen from Table 3 that the excess entropy due to charging process, cancels the entropy S_{hs} of neutral hard-sphere mixtures partly and the ratio $|S_{ch}|/S$ is 0.38 at 50 at % of Cs, whereas it is 0.1 at 80 at % of Cs, indicating that the charge-ordering process decreases with the increase of Cs-concentration. Figure 4 shows that the entropy due to Coulomb interaction is

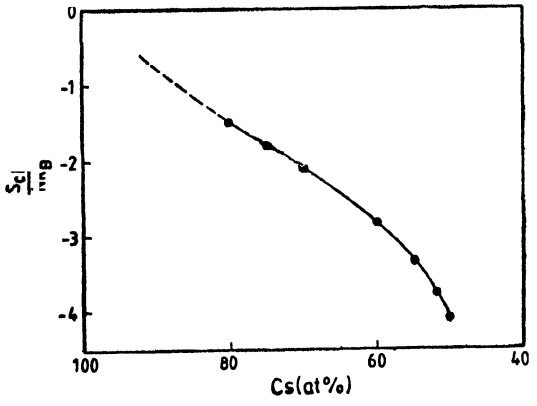

Figure 4. Entropy due to Coulomb interaction at different at % of Cs.

maximum at 50 at % of Cs and it is in accordance with the experiment (Schmultzler *et al* 1976, Freyland and Steinleitner 1976, Martin *et al* 1980). It is also clear from Table 3 that the excess internal energy E^{ex} and Helmholtz free energy F^{ex} is contributing large amount due to Coulomb interactions. Another point may be mentioned that the magnitude of the excess energy per particle gives a quantitative understanding of the inter-ionic stability of the molten alloys at different at % of Cs.

The quantity obtained by experiment is not the entropy itself but the entropy of mixing ΔS, which is defined by

$$\Delta S = S - C_{Cs}S_{Cs} - C_{Au}S_{Au}. \tag{23}$$

Here, the experimental determination of ΔS has some difficulties (Hoshino 1984), hence the theoretical evaluation of an entropy becomes very important, Au at 913° K is a solid and we use as Hoshino (1984) the extrapolated value of 10.22 Hultgren *et al* 1973 and evaluate $\Delta S/Nk_B$ at 50 at % of Cs, and this value is found to be -2.27 and is in good agreement with that found by Hoshino (1984) who used Waisman-Lebowitz equations (Waisman and Lebowitz 1972) for equal diameters of Cs^+ and Au^--ions.

The present method using Blum's equations appear to yield good structural results and offer a method of evaluating structural and thermodynamic properties of charge transfer alloys along with the molten salts (Rao and Satpathy 1988, 1989). In addition, Blum's method uses the smallest number of parameters, namely, the molecular diameters even when the diameters of the species of the alloy are not equal.

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